# EFFECT OF NONSOLVENT ADDITIVE ON DEVELOPMENT OF POLYETHERSULFONE (PES) MEMBRANE FOR $O_2/N_2$ SEPARATION

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## ABSTRACT

The objectives of this study are to develop new dope formulation for producing asymmetric membrane for $O_2/N_2$ separation by using three different types of nonsolvent additives (NSA). Polyethersulfone (PES) asymmetric flat sheet membrane was prepared by the dry/wet phase inversion process from casting solution containing polyethersulfone (PES) as polymer, 1-methyl-2-pyrrolidone (NMP) as solvent and three different types of NSA which are water, ethanol, and methanol. The casting solutions were casted using manually casting technique. Then, the membranes were coated with silicone polymer in order to improve the membrane surface. The membranes were tested using $O_2$ and $N_2$ gases permeation test system. The morphologies of the membranes were then examined by using scanning electron microscopy (SEM). Consequently, from the pure gas permeation test results, it was found that the optimum weight percent solution containing the best nonsolvent were 27.24%wt of PES, 64.72%wt of NMP and 7.54%wt of $H_20$. SEM results showed the different NSA used will produce different influence on gas separation characteristics and morphologies of the produced membranes. The newly developed PES membranes with new casting solution formulation that used $H_2O$ as NSA, resulted $O_2/N_2$ selectivity of 3.22 and permeability of $O_2$ gas was 11.97 GPU and permeability of $N_2$ gas was 3.71 GPU. Addition of $H_2O$ as NSA resulted the lowest skin thickness compared to EtOH and MeOH which 781.5nm. Thicker of skin thickness of membranes means the chance of pinhole formation seems to be least which was contributed to high permeation of $O_2$ gas and low permeation of $N_2$ gas. Therefore, the PES membranes prepared from NMP/$H_2O$ proved to provide the best separation characteristics compared to those membranes produced from NMP/EtOH solvent and NMP/MeOH solvent system. As a conclusion, it should be emphasized that the membrane of the highest flux and highest selectivity could be obtained by proper adjustment of the skin layer thickness and the sub layer morphology which was done by proper choice of nonsolvent additive. Thus, choosing the best nonsolvent additive had successfully developed asymmetric PES membranes for $O_2/N_2$ separation applications.

## ABSTRAK

Objektif penyelidikan ini adalah untuk menghasilkan satu jenis formulasi berprestasi tinggi dan bebas kecacatan menggunakan membran asimetrik polyethersulfona (PES) bagi proses pemisahan $O_2/N_2$. Membran PES kepingan rata dihasilkan melalui hasil proses fasa balikan kering/basah yang mengandungi 1-methyl-2-pyrrolidona (NMP) digunakan sebagai pelarut, menggunakan tiga bahan tambah bukan pelarut (NSA) iaitu air suling ($H_2O$), ethanol (EtOH), dan methanol (MeOH). Membran asimetrik kepingan rata dihasilkan menggunakan cara penuangan manual dan membrane disalut menggunakan silikon untuk meningkatkan prestasi permukaan membran dan kadar ketelapan membran diuji menggunakan mesin ujian kebolehtelapan gas tulen menggunakan mikroskop pengimpasan elektron (SEM). Keputusan kajian menunjukkan bahawa peratus berat optimum yang mengandungi NSA terbaik adalah 27.24%wt PES, 64.72%wt NMP dan 7.54%wt $H_2O$. Keputusan SEM menunjukkan bahawa NSA yang berbeza akan menghasilkan pengaruh yang berbeza pada ciri-ciri pemisahan gas dan struktur membran yang dihasilkan. Membran yang telah dihasilkan dengan formulasi yang baru yang menggunakan $H_2O$ sebagai NSA menunjukkan kememilihan $O_2/N_2$ dan fluks tekanan-ternormal ialah 3.224 dengan kadar ketelapan gas $O_2$ adalah 11.97 GPU dan kadar ketelapan gas $N_2$ adalah 3.71 GPU. Penambahan $H_2O$ sebagai NSA menghasilkan ketebalan kulit terendah berbanding dengan EtOH dan MeOH iaitu bernilai 781.5nm. Semakin tebal kulit selaput bererti pembentukan lubang jarum yang terhasil adalah sedikit yang boleh disumbangkan untuk kualiti ketelapan $O_2/N_2$ yang rendah. Oleh kerana itu, membran PES dihasilkan dari NMP/$H_2O$ terbukti memberikan ciri-ciri pemisahan yang lebih baik berbanding dengan membran yang dihasilkan dari NMP/EtOH dan NMP/MeOH sistem pelarut. Kesimpulannya,membran fluks yang tertinggi dan kememilihan tertinggi boleh diperolehi dengan perubahan yang tepat dari ketebalan lapisan kulit dan lapisan struktur membran yang dilakukan oleh pilihan bahan tambah bukan pelarut yang tepat. Oleh itu, pemilihan NSA terbaik telah berjaya meningkatkan prestasi membran, menghasilkan membran bebas kecacatan dan menghasilkan kulit lapisan tipis untuk membran asimetrik untuk pemisahan $O_2/N_2$.

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# LIST OF SYMBOLS

| | | |
|---|---|---|
| $O_2$ | : | Oxygen |
| $N_2$ | : | Nitrogen |
| °C | : | Celsius |
| α | : | Selectivity |
| *d* | : | Kinetic diameter |
| *Ji* | : | Flux of the component i |
| *Di* | : | Diffusion coefficient ($cm^2/s$) |
| *Si* | : | Effective solubility coefficient ($cm^3$ (STP)/$cm^3$.cm.Hg) |
| *ki* | : | Solubility constant |
| *Pi* | : | Partial pressure (cm Hg) |
| Å | : | Amstrong |
| cP | : | Centrepoise |
| Tg | : | Glass transition temperature |
| *P* | : | Permeability coefficient of gas($cm^3$(STP)cm/$cm^2$.s.cmHg) |
| Q | : | Volumetric flow rate of gas ($cm^3/s$) at STP |
| A | : | Membrane structure area ($cm^2$) |
| *l* | : | Membrane thickness or skin layer thickness (cm) |
| (P/*l*) | : | Pressure–normalized flux ($cm^3$ (STP)/ $cm^2$. s. cm Hg) |
| P | : | Pressure |
| T | : | Temperature |
| μm | : | Micrometer |

# LIST OF ABBREVIATIONS

| | | |
|---|---|---|
| NSA | : | Nonsolvent Additive |
| SEM | : | Scanning Electron Microscope |
| PES | : | Polyethersulfone |
| NMP | : | N-Methyl-Pyrrolidon |
| MW | : | Molecular Weight |
| GPU | : | Gas permeation unit |
| EtOH | : | Ethanol |
| $H_2O$ | : | Water |
| MeOH | : | Methanol |
| DA | : | Diffusivity selectivity A |
| DB | : | Diffusivity selectivity B |
| SA | : | Solubility selectivity A |
| SB | : | Solubility selectivity B |
| FTIR | : | Fourier Transform Infrared Spectroscopy |

# CHAPTER 1

# INTRODUCTION

## 1.1 RESEARCH BACKGROUND

According to Pinnau and Freeman, a membrane is a thin barrier that permits selective mass transport which can be fabricated from a wide variety of organic (e.g. polymers, liquid) or inorganic (e.g. carbons, zeolites etc) materials (Pinnau and Freeman, 2000). Currently, the vast majority of commercial membranes are made from polymers and the properties of the membrane are controlled by the material and membrane structure. Baker stated that a membrane is nothing more than a discrete, thin interface that moderates the permeation of chemical species in contact with it and by referred to Mark, a synthetic membrane is a barrier which separates two phases and restricts the transport of various chemical species in a rather species manner which membrane can be homogeneous or heterogeneous, symmetric or asymmetric in structure; it may be solid or liquid; it may be neutral, may carry positive or negative charges, or may be bipolar (Baker,2000 and Mark,1990).

Polymeric materials are still the most widely used membranes for gas separation (Pabby *et al*, 2009). Asymmetric membranes are mostly produced by the method namely the dry and wet method (Li *et al*, 2008). Gas separation processes require a membrane with high permeability and high selectivity (Lin *et al*, 1996).

The addition of a suitable nonsolvent additive into the membrane casting solution accelerates the coagulation process from solution to gel when the casting solution was immersed in a coagulant which results membranes with thinner skin layer and more uniform structure (Dongliang *et al*, 1995). The different additives have

distinctive effects on dope viscosity but their individual effects on inherent viscosity are surprising similar (Na *et al*, 2009).

According to the previous researches, they observed that the membrane selectivity tends to decrease as the nodule size at the membrane surface become larger or the roughness of the membrane surface increases. He found that the membrane that contained 2-ethyl-1-hexanol as its additive had the highest permeance ratio, selectivity, α $O_2/N_2$ is 5.5 and the lowest mean diameter, 27.8nm which smaller nodules resulted in higher permeance ratio (Tan *et al*, 1999).

For TPX membranes, additives such as n-propanol, n-butanol, cyclohexanol, acetic acid and 1-methyl-2-pyrrolidone (NMP) can successfully increase the membrane porosity. In fact, not only the porosity but also the membrane morphology is influenced by the addition of nonsolvent (Juin *et al*, 1996). Besides, by adding nonsolvent, membrane formation mechanism changed from polymer crystallization to liquid-liquid phase separation. By increasing the nonsolvent concentration, interaction between polymer and mixture of solvent and nonsolvent became worse and cloud point temperature increased (Saeid *et al* 2008).

Norida found that by using water as nonsolvent additive, at evaporation rate 8 seconds and membrane is coated, the selectivity of $O_2/N_2$ is low which 5.12 with high permeability of $N_2$ which 2.03 and $O_2$ which 10.32. Meanwhile, at evaporation rate is 20 seconds, when selectivity of $O_2/N_2$ is high, which 11.79, the permeability of $N_2$ and $O_2$ will be low which 0.63 for $N_2$ and 7.30 for $O_2$. By using ethanol as nonsolvent additive, membrane is coated and at evaporation rate is 8 seconds, $O_2/N_2$ produce low selectivity which 4.42 while the permeability of $N_2$ and $O_2$ both high which 3.28 and 14.29 respectively. In contrast, at evaporation time is 20 seconds, the selectivity is high which 5.77 while the permeability of $N_2$ is 1.26 and permeability of $O_2$ is 7.26 (Norida, 2004).

So, this can conclude that addition of nonsolvent additive influence the permeability of $O_2/N_2$ hence contribute to change the membrane selectivity.

## 1.2 PROBLEM STATEMENT

One of the major problems confronting the use of membrane based separation processes in a wide range of applications is the lack of membranes with high flux and high selectivity. During fabrication, membrane formation process plays an important role and certain factors need proper attention in order to produce a good separation membrane. In this research the different types of nonsolvent additive (NSA) will be used to produce high selectivity and high permeability.

Previous research showed that by using different type of NSA will produce different permeability results and membrane morphology. Therefore, in this study, the aim is to get membrane with high permeability and selectivity by changing the membrane morphology in order to get defect free membrane.

## 1.3 OBJECTIVES OF THE RESEARCH

Based on the problem statement described in the previous section, the following are the objectives of this research:

1. Developing new types solution formulation asymmetric polyethersulfone membrane for gas separation application.

## 1.4 SCOPES OF THE RESEARCH

1. To develop different type of solution formulation by varying the different type of nonsolvent additives (NSA) for the development of high performance and polyethersulfone membrane.
2. Characterization of uncoated membrane and coated by using pure gases $N_2$ and $O_2$ as test gases to determine their performances.
3. Morphological studies of the surface layer and cross section of the developed membrane using Scanning Electron Microscopy (SEM).

## 1.5 RATIONALE AND SIGNIFICANCE

Polyethersulfone (PES) has been chosen as the polymer membranes as it has good process ability, inexpensive production and low operating cost and modular design. In short, it offer low capital cost, low energy consumption, ease of operation and cost effectiveness. Besides, membrane with higher permeability leads to higher productivity and lower capital cost whereas membrane with higher selectivity leads to more efficient separations, higher recovery and lower power cost.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 MEMBRANE SEPARATION TECHNOLOGY

According to Freeman and Pinnau, separation of gases using polymer membranes is an important unit operation that competes effectively with well-established processes such as cryogenic distillation, absorption and pressure-swing adsorption. Commercially, the most widely practiced gas separations using membranes are the production of high purity nitrogen from air, recovery of hydrogen from mixtures with larger components such as nitrogen, methane, and carbon monoxide, and purification of natural gas by removal of carbon dioxide. In these separations, membranes with adequately high fluxes of the more permeable components (oxygen, hydrogen, and carbon dioxide, respectively) and sufficient selectivity have been developed for membranes to be competitive with other gas separation technologies. The membrane materials used in these separations are glassy polymers, which derive high selectivity in large measure from their ability to separate gases based on subtle differences in penetrant size. Such polymers are most permeable to the smallest components in a mixture and least permeable to the largest components (Freeman and Pinnau, 1999).

Membranes with higher selectivity are desirable because higher product purity can be achieved in a separation process. Typically, porous membranes are used in dialysis, ultrafiltration, and microfiltration applications. Optimum porous membranes have high porosity and a narrow pore size distribution. Membranes having a dense, selective layer are applied in reverse osmosis, pervaporation, and gas separation processes. Permeation through dense membranes occurs by a solution/diffusion

mechanism. Ideal dense membranes should have a very thin selective layer, because flux is inversely proportional to the membrane thickness. In addition, the thin separating layer should be molecularly dense, because even a very small area fraction of defects in the membrane can cause a significant decrease in selectivity (Pinnau and Freeman, 2000). Table 2.1 show the common polymer used for production of commercial membranes.

**Table 2.1:** Common Polymers Used for Production of Commercial Membranes (Pinnau and Freeman, 2000)

| Membrane Processes | Membrane Material |
|---|---|
| Microfiltration | Cellulose regenerated, cellulose nitrate, cellulose acetate, polyamide, polysulfone, poly(ether sulfone), polycarbonate, poly(ether imide), poly(vinylidene fluoride), polytetrafluoethylene, polypropylene, polyarcylonitrile |
| Ultrafiltration | Celulose regenerated, cellulose acetate, polyamide, polysilfone, poly(ether sulfone), polycarbonate, poly(ether imide), poly(vinylidene fluoride), polyacrylonitrile, poly(methyl methacrylate) |
| Nanofiltration | Polyamide |
| Dialysis | Cellulose regenerated, cellulose acetate, polyamide, polycarbonate, polyacrylonitrile, poly(methyl methacrylate) |
| Pervaporation | Poly(vinyl alcohol), polydimethylsiloxane |
| Gas Separation | Polysulfone, polycarbonate, poly(2,6-dimethyl-1,4-phenylene oxide), polyimide, polydimethylsiloxane |

During the past few decades, membrane separation process has become one of the emerging technologies that underwent a rapid growth. It has drawn the attention of researchers in the separation technology field with its better performance compared to the conventional separation technology (Shin *et al*, 2008). The main membrane separation technologies include microfiltration, ultrafiltration, reverse osmosis and nanofiltration, electrodialysis, gas separation and pervaporation (Baker, 2004). Table 2.2 shows the summary of the established membrane separation technologies.

**Table 2.2:** Summary of the established membrane separation technologies (Baker, 2004)

| Process | Principle | Type of Membrane | Initial of Feed Phase | Driving Force | Industrial Applications |
|---|---|---|---|---|---|
| Microfiltration | Separation of organic and polymeric compounds with micropore ranges of 0.1-10μm | Finely microporous 0.1-10μm | Liquid or gas | Pressure Difference 35-350kPa | Removal of suspended solids, bacteria in pharmaceutical, electronics industries |
| Ultrafiltration | Separation of water and microsolutes from macromolecules and colloids | Finely microporous 1-100nm | Liquid | Pressure Difference 140-700kPa | Removal of colloidal material from wastewater, and food process streams |
| Reverse Osmosis | Passage of solvents through a dense membrane that is permeable to solvents but not solutes | Dense solution-diffusion | Liquid | Pressure Difference 700-7000kPa | Drinking water from sea, brakish or groundwater; production of ultra-pure water for electronics and pharmaceutical industries |
| Electrodialysis | Ions are transported through a membrane from one solution to another under the influence of an electrical potential | Electrically charged films | Liquid | Voltage difference 1-2V | De-ionized water from conductive spacers, recovery of organic acids from, heavy metal recovery |
| Gas Separation | Component of mixture of gaseous is removed through a pressure gradient | Dense solution-diffusion | Vapor or gas | Pressure difference 700-7000kPa | Removal of nitrogen from air, hydrogen from petrochemical/refinery vents, carbon dioxide from natural gas, propylene and VOCs from petrochemical vents |
| Pervaporation | Component of a mixture diffuses through, evaporates under a low pressure and is removed by a vacuum | Dense solution-diffusion | Liquid | Vapor pressure 7-70Kpa | Dehydration of solvents, separation of azeotropic mixtures |

## 2.2 HISTORICAL BACKGROUND AND CURRENT STATUS OF THE TECHNOLOGY

Table 2.3 below represented the sequences of the history membrane process development.

**Table 2.3:** Historical Background and Current Status (Baker, 2000)

| Year | Name of Scientist | Systematic Studies |
|---|---|---|
| 1974 | Abbe Nolet | • Coined the word 'osmosis' to describe permeation of water through a diaphragm. |
| $19^{th}$ –early $20^{th}$ centuries | - | • Membranes had no industrial or commercial uses but were used as laboratory tools to develop physical/chemical theories. |
| 1887 | Traube and Preffer | • Explains the behaviour of either dilute solution. |
| 1907 | Bechhold | • Devised a technique to prepare nitrocellulose membranes of graded pore size, which he determined by a bubble test. |
| - | Elford,Zsigmondy, Bachmann and Ferry | • Improved on Bechhold's technique. |
| 1930s | - | • Microporous collodion membranes were commercially available. |
| 1945 | W.J.Kolf | • Had demonstrated the $1^{st}$ successfully artificial kidney in The Netherland ( use of membranes in artificial organ )<br>• This development was complete by early 1960s. |
| 1950s | - | • The early microfiltration membrane technology was expanded to other polymers, notably cellulose acetate.<br>• Membranes found their $1^{st}$ significant application in the testing of drinking water at the end of World War 2. |
| 1960 | - | • The elements of modern membrane science had been developed but membranes were used in only a few laboratory and small, specialized industrial applications.<br>• No significant membrane industry existed because too unreliable, slow, unselective and expensive. |

| Year | Name of Scientist | Systematic Studies |
|---|---|---|
| Early 1960s | Loeb-Sourirajan | • Making defect-free, high flux, anisotropic reverse osmosis membranes.<br>• This membrane consist of an ultrathin, selective surface film on a much thicker but much more permeable microporous support which provide mechanical strength. |
| 1966 | Alex Zaffaroni | • Development of the membrane blood oxygenator for controlled drug delivery systems.<br>• Widely used in pharmaceutical industry to improve the efficiency and safety of drug delivery. |
| 1980s | - | • Microfiltration, ultrafiltration, reverse osmosis and electrodialysis were all established processes with large plants installed worldwide. |
| | - | • The emergence of industrial membrane gas separation processes.<br>• 1st major development was the Monsanto Prism membrane for hydrogen separation. |
| | Dow | • Producing systems to separate nitrogen from air. |
| | Cynara and Separex | • Producing systems to separate carbon dioxide from natural gas. |
| | GFT company ( a small German engineering company) | • 1st commercial pervaporation systems for dehydration alcohol. |

Table 2.4 below lists the development of technically for some membrane processes.

**Table 2.4:** Development of (technical) membrane processes (Marcel, 1996)

| Membrane Process | Country | Year | Application |
|---|---|---|---|
| Microfiltration† | Germany | 1920 | Laboratory use (bacterial filter) |
| Ultrafiltration† | Germany | 1930 | Laboratory use |
| Hemodialysis† | Netherlands | 1950 | Artificial kidney |
| Electrodialysis# | USA | 1955 | Desalination |
| Reverse Osmosis# | USA | 1960 | Sea water desalination |
| Ultrafiltration# | USA | 1960 | Concentration of macromolecules |
| Gas Separation# | USA | 1979 | Hydrogen recovery |
| Membrane Distillation† | Germany | 1981 | Concentration of aqueous solutions |
| Pervaporation# | Germany/Netherlands | 1982 | Dehydration of organic solvents |

† Small scale

# Industrial scale

## 2.3 ADVANTAGES OF MEMBRANE TECHNOLOGY

Membrane separation processes are highly innovative process engineering operations. Certain types of materials are inherently difficult and expensive to be separated. Hence, membrane technology would be promising in the future and can offer an alternative to the conventional industrial separation methods. Recently, membrane separation processes are increasingly important and popular in industries and have become attractive alternatives to conventional methods such as absorption, distillation, extraction, leaching, crystallization and adsorption etc. They offer a number of significant advantages and attractions over competing technologies.

Membrane nowadays have gained wide acceptance and made significant inroads against competing technologies in many areas because of flexibility and performance reliability of membrane system, cost competitiveness, increasing demand and environmental awareness. Besides that, the advantages using polymer membranes are

good processability, inexpensive production and low operating cost (relatively low capital and running costs) and modular design (construction). In short, they offer low capital cost, low energy consumption, ease of operation and cost effectiveness.

## 2.4 SOLUTION-DIFFUSION MECHANISM

Solution-diffusion separation is based on both solubility and mobility factors. Diffusity favors the smallest molecules while solubility selectivity favors the most condensable one (Norida, 2004). Diffusion, the basis of the solution-diffusion model, is the process by which matter is transported from one part of a system to another by a concentration gradient (Baker, 2000).

The diffusion can be defined as a relationship wherein the flux of a diffusing species is proportional to the concentration gradient by Fick's first law (Baker, 2000).

$$J_x = -D\frac{dC}{dx} \qquad \text{Equation 2.1}$$

where,

$J_x$ = the flux of the diffusing species (g/cm$^2$.s)
$dC/dx$ = the incremental change in concentration with distance
$D$ = diffusivity or diffusion coefficient = the proportionality constant (cm$^2$/s)

The solubility of a gas in a liquid is directly proportional to the gas pressure. This is a statement of Henry's Law, (Kotz *et al*, 2009).

$$S_g = K_H . P_g \qquad \text{Equation 2.2}$$

where, $S_g$ is the gas solubility, $P_g$ is the partial pressure of the gaseous solute, and $K_H$ is Henry's Law constant, Table 2.5 shows a constant characteristic of a solute and solvent.

**Table 2.5**: Henry's Law constant ($25^0$C)

| Gas | $K_H$ (mol/kg.bar) |
|---|---|
| $N_2$ | $6.0x10^{-4}$ |
| $O_2$ | $1.3x10^{-4}$ |
| $CO_2$ | 0.034 |

Predicting membrane permeability can be divided into two parts because permeability is the product of the diffusion coefficient and the sorption coefficient (Baker, 2000).

$$P=D.K \quad \text{-------►} \quad \text{Equation 2.3}$$

where P is permeability, K is the sorption coefficient and D is diffusion coefficient.

James state that the equilibrium concentration (solubility), c, of a penetrant gas dissolved in a polymer can be related to the pressure, p, of the penetrant by the isothermal relation:

$$c = S(c).p \quad \text{-------►} \quad \text{Equation 2.4}$$

where, S(c) [or S (p)] is a solubility coefficient (James, 2007).

According to Ismail and Lai, 2004, for the gas permeation measurement, gas permeation rate can be calculated by,

$$\left(\frac{P}{l}\right)_i = \frac{Q_i}{A\,\Delta p} \quad \text{-------►} \quad \text{Equation 2.5}$$

where (P/*l*)*i* is defined as pressure-normalized flux or permeability for gas *i*. The common unit of pressure-normalized gas flux is GPU (1GPU=1X$10^{-6}$ $cm^3$ (STP) $cm/cm^2$.s.sm.Hg. Q*i* is volumetric flow rate of gas *i*, Δp the pressure difference across

membrane, A the membrane effective surface area and *l* the membrane skin thickness. (Ismail and Lai, 2004). Selectivity (unitless) of asymmetric membrane can be determined by,

$$\alpha_{ij} = \frac{P_i}{P_j} = \frac{(P/l)_i}{(P/l)_j}. \qquad \text{Equation 2.6}$$

Total gas flux through asymmetric polymeric membrane with defects is sum of permeation through polymeric material of skin layer and flux through defects. The former is exclusively predominated by solution-diffusion mechanism, while the latter occurs due to the combination of Knudsen diffusion, viscous diffusion and/or bulk diffusion (Marchese and Pagliero, 1994).

For simplicity in evaluation of skin structural parameters, following assumptions were made and stated as below (Ismail and Lai, 2004):

a) Asymmetric membrane consists of a skin of uniform thickness supported on a porous sublayer. The skin represents the actual separating barrier, while the sublayer serves only as a mechanical support, with negligible effects on separation (with negligible substructure resistance).
b) Contribution of gas flux permeating through dense skin is greater than 10% of slip flux in pore (defects).
c) Gas permeation through asymmetric membrane is assumed a steady-state mode.
d) Intrinsic permeability (and selectivity) is taken as being independent of pressure in experimental range of exploration (200-450cmHg).
e) Downstream pressure is negligible if compared to upstream pressure.

## 2.5 ASYMMETRIC MEMBRANE

Asymmetric membranes are mostly produced by dry/wet phase inversion method comprised of these steps (Li *et al*, 2008):

a) Preparation of the polymer solution called dope.
b) Molding (cast or spinning) of the dope.
c) Coagulation of the dope by contact with nonsolvent of the polymer to form the asymmetric structure.
d) Drying of the coagulated membrane.

Membranes can be produced in flat sheet or tubular (hollow-fiber) geometry. Flat sheet membranes are packaged either in plate and frame or spiral wound modules, whereas tubular membranes are packaged in hollow fiber modules. Although hollow fiber modules have highest membrane packing density per module volume, spiral wound and plate and frame modules are also commonly used in large scale separation processes.

Membranes either have a symmetric (isotropic) or an asymmetric (anisotropic) structure. Symmetric membranes have a uniform structure throughout the entire membrane thickness, whereas asymmetric membranes have a gradient structure. The separation properties of symmetric are determined by their entire structure. On the other hand, the separation properties of asymmetric membrane are determined primarily by the densest region in the membrane. The most common symmetric and asymmetric membrane types are shown in Figure 2.1 (Pinnau and Freeman, 2000):